

Oxo and imido/imido exchange and C–H activation reactions based on pentamethylcyclopentadienyl imido tantalum complexes

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This paper is dedicated to Professor S. Pasynkiewicz on the occasion of his 70th birthday

Abstract

Reactions of $[\text{TaCp}^*\text{Cl}_4]$ with two, three and four equivalents of $\text{LiNH}'\text{Bu}$ give the halo- and amido-imido complexes $[\text{TaCp}^*\text{Cl}_2(\text{N}'\text{Bu})]$ (**1a**), $[\text{TaCp}^*\text{Cl}(\text{N}'\text{Bu})(\text{NH}'\text{Bu})]$ (**2**) and $[\text{TaCp}^*(\text{N}'\text{Bu})(\text{NH}'\text{Bu})_2]$ (**3**), respectively. The related complex $[\text{TaCp}^*\text{Cl}_2\{\text{N}(2,6\text{-Me}_2\text{C}_6\text{H}_3)\}]$ (**1b**) is prepared by a similar reaction using two equivalents of $\text{Li}[\text{NH}(2,6\text{-Me}_2\text{C}_6\text{H}_3)]$. Complex **3** can be transformed into **2** and further into **1a** by reaction with SiClMe_3 . Complex **1a** reacts with $\text{CN}'\text{Bu}$ to give the 18-electron adduct $[\text{TaCp}^*\text{Cl}_2(\text{N}'\text{Bu})(\text{CN}'\text{Bu})]$ (**4**) whereas addition of excess $\text{CN}(2,6\text{-Me}_2\text{C}_6\text{H}_3)$ results in reductive elimination of the carbodiimide $\text{'BuN}=\text{C}=\text{N}(2,6\text{-Me}_2\text{C}_6\text{H}_3)$ (**5**) to give $[\text{TaCp}^*\text{Cl}_2\{\text{CN}(2,6\text{-Me}_2\text{C}_6\text{H}_3)\}_3]$. However complex **1b** does not react with any of the isocyanide ligands. Both complexes **1a** and **1b** react with PhCHO undergoing imido/oxo exchange to give the imines $\text{PhCH}=\text{NR}$ ($\text{R} = \text{'Bu}$, $2,6\text{-Me}_2\text{C}_6\text{H}_3$ (**6**)) and dimeric $[\text{TaCp}^*\text{Cl}_2(\text{O})]_2$ or trimeric $[(\text{TaCp}^*\text{Cl})_3(\mu_2\text{-Cl})(\mu_2\text{-O})_3(\mu_3\text{-O})]$ oxo-complexes, whereas only **1a** reacts with CO_2 , $\text{PhCH}=\text{NR}'$ ($\text{R}' = \text{Ph}$, Me) and $(2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{N}=\text{C}=\text{N}'\text{Bu}$ producing $\text{'BuN}=\text{CO}$, $\text{PhCH}=\text{N}'\text{Bu}$ and $\text{'BuN}=\text{C}=\text{N}'\text{Bu}$, respectively and the corresponding oxo or imido tantalum derivative. None of the complexes reacts with CO or NCR ($\text{R} = \text{Me}$, Ph). The complex $[\text{TaCp}^*\text{Me}(\text{N}'\text{Bu})(\text{NH}'\text{Bu})]$ activates C–H bonds when heated in benzene and toluene affording $[\text{TaCp}^*\text{Ph}(\text{N}'\text{Bu})(\text{NH}'\text{Bu})]$ (**7**) and a mixture of $[\text{TaCp}^*(m\text{-MeC}_6\text{H}_4)(\text{N}'\text{Bu})(\text{NH}'\text{Bu})]$ (**8a**) and $[\text{TaCp}^*(p\text{-MeC}_6\text{H}_4)(\text{N}'\text{Bu})(\text{NH}'\text{Bu})]$ (**8b**). All of the reported organic compounds and tantalum complexes were characterized by ^1H - and ^{13}C -NMR spectroscopy. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Oxo/imido imido/imido exchange; C–H activation; Cyclopentadienyl imido tantalum complexes

1. Introduction

Interest in the synthesis and isolation of transition metal imido [1] complexes was prompted by the use of imido substituents as ‘protecting ligands’ in many early transition metal alkylidene complexes, extensively applied as catalysts in olefin metathesis [2] and ring-opening metathesis polymerization [3] processes. However, the imido group is not only an unreactive spectator ligand but a highly nucleophilic center which can react with metal coordinated unsaturated molecules to which the imido group is easily transferred. This reaction is the basis for many catalytic and stoichiometric pro-

cesses [4] of great interest in organic synthesis using imido complexes of the late and early transition metals. Trapping reactions of the imidozirconocene complex $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\text{N}'\text{Bu})]$, its reactions with isocyanides and isobutylene oxide and many applications in the metathesis of ketones, imines, isocyanates, [2 + 2] cycloadditions of olefins and alkynes and [2 + 3] cycloadditions of azides have been extensively reported [5]. Studies with related molybdenum complexes have also been reported for the metathesis of carbodiimides and isocyanates [6a,b] and more recently for the catalytic metathesis of imines [6c,d], trying to avoid competing dimerization processes that would deactivate the zirconium catalyst or high concentrations of imine that would inhibit it. Imido titanium [7] and zirconium [5c,8] complexes have been shown to activate the carbon–hydrogen bond of hydrocarbons. Fewer studies have been reported for [2 + 2] cycloaddition or carbon–hydrogen

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bond activation reactions of imido vanadium [9] [10] and tantalum [11] complexes. We reported [12] several reactions giving imido tantalum complexes and the conversion of an imido acyl complex into the oxo iminoacyl derivative.

This article describes the results of our work on the reactivity of imido tantalum complexes $[\text{TaCp}^*\text{Cl}_2(\text{NR})]$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$; $\text{R} = \text{'Bu}$ (**1a**), 2,6- $\text{Me}_2\text{C}_6\text{H}_3$ (**1b**)) with various unsaturated compounds including isocyanides CNR ($\text{R} = \text{'Bu}$, 2,6- $\text{Me}_2\text{C}_6\text{H}_3$), benzaldehyde PhCHO , imines PhCHNR ($\text{R} = \text{Ph}$, Me), carbodiimides $\text{'BuNCN(2,6-Me}_2\text{C}_6\text{H}_3)$ and CO_2 , as well as the carbon–hydrogen bond activation of benzene and toluene by the methyl complex $[\text{TaCp}^*\text{Me(N'Bu)(NH'Bu)}]$.

2. Results and discussion

2.1. Synthesis of imido complexes

We were looking for a convenient method to prepare a series of chloro-amido imidotantalum complexes avoiding the method used to isolate $[\text{TaCp}^*\text{Cl}_2(\text{N'Bu})]$ [13], which is rather tedious when bulk quantities of this product are required. We decided to go in the reverse direction starting from the totally amidated compound and exchanging amido for chloro substituents [14].

The reaction of $[\text{TaCp}^*\text{Cl}_4]$ with four equivalents of LiNH'Bu in ethyl ether at room temperature provides a good method to isolate $[\text{TaCp}^*(\text{N'Bu})(\text{NH'Bu})_2]$ (**3**) as a colorless solid in 85% yield (see Scheme 1). The same reaction carried out with three equivalents of LiNH'Bu gave the chloro amido complex

$[\text{TaCp}^*\text{Cl}(\text{N'Bu})(\text{NH'Bu})]$ (**2**), isolated as a spectroscopically pure yellow oil, whereas addition of only two or one equivalents of LiNH'Bu afforded a mixture containing variable amounts of **2**, $[\text{TaCp}^*\text{Cl}_2(\text{N'Bu})]$ (**1a**) and small amounts of other unidentified products.

The same reaction using different lithium amides was reported to afford other monocyclopentadienyl imidotantalum complexes [15]. We also used this procedure to isolate the previously reported [12c] $[\text{TaCp}^*\text{Cl}_2\{\text{N(2,6-Me}_2\text{C}_6\text{H}_3)\}]$ (**1b**) from the reaction of an ethyl ether suspension of $[\text{TaCp}^*\text{Cl}_4]$ with two equivalents of $\text{Li[NH(2,6-Me}_2\text{C}_6\text{H}_3)]$ to give **1b** as an orange solid in 81% yield.

A preliminary reaction monitored by $^1\text{H-NMR}$ spectroscopy revealed that addition of one equivalent of SiClMe_3 transformed the diamido complex $[\text{TaCp}^*(\text{N'Bu})(\text{NH'Bu})_2]$ (**3**) into the chloro-amido derivative $[\text{TaCp}^*\text{Cl}(\text{N'Bu})(\text{NH'Bu})]$ (**2**) with elimination of $\text{SiMe}_3(\text{NH'Bu})$, and further addition of a second equivalent quantitatively converted **2** into the dichloro compound $[\text{TaCp}^*\text{Cl}_2(\text{N'Bu})]$ (**1a**), which was stable in the presence of excess SiClMe_3 .

These observations were used to develop a convenient method to prepare $[\text{TaCp}^*\text{Cl}_2(\text{N'Bu})]$ (**1a**) by reacting an ethyl ether suspension of $[\text{TaCp}^*\text{Cl}_4]$ with more than two equivalents of LiNH'Bu , followed by the addition of excess SiClMe_3 to give **1a** as a yellow oil in 72% yield.

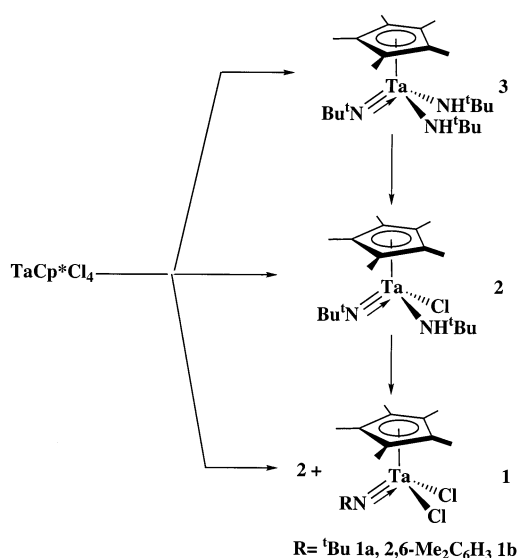
The presence of the amido and imido groups in compounds **1–3** can be easily assigned from the $^{13}\text{C-NMR}$ resonance due to the quaternary carbon of the 'Bu group, which was observed at ca. δ 55 for the amido NH'Bu and at ca. δ 65 for the imido N'Bu groups. Moreover, the $^1\text{H-NMR}$ spectra showed the resonance due to the amido proton for **2** and **3** at δ 5.64 and δ 3.01 (two protons) respectively, indicating a higher π -bonding contribution from the amido group in **2** with its more electronegative chloro substituent.

All of the complexes **1–3** were thermally stable and water sensitive although they could be stored unaltered for long periods under an inert atmosphere.

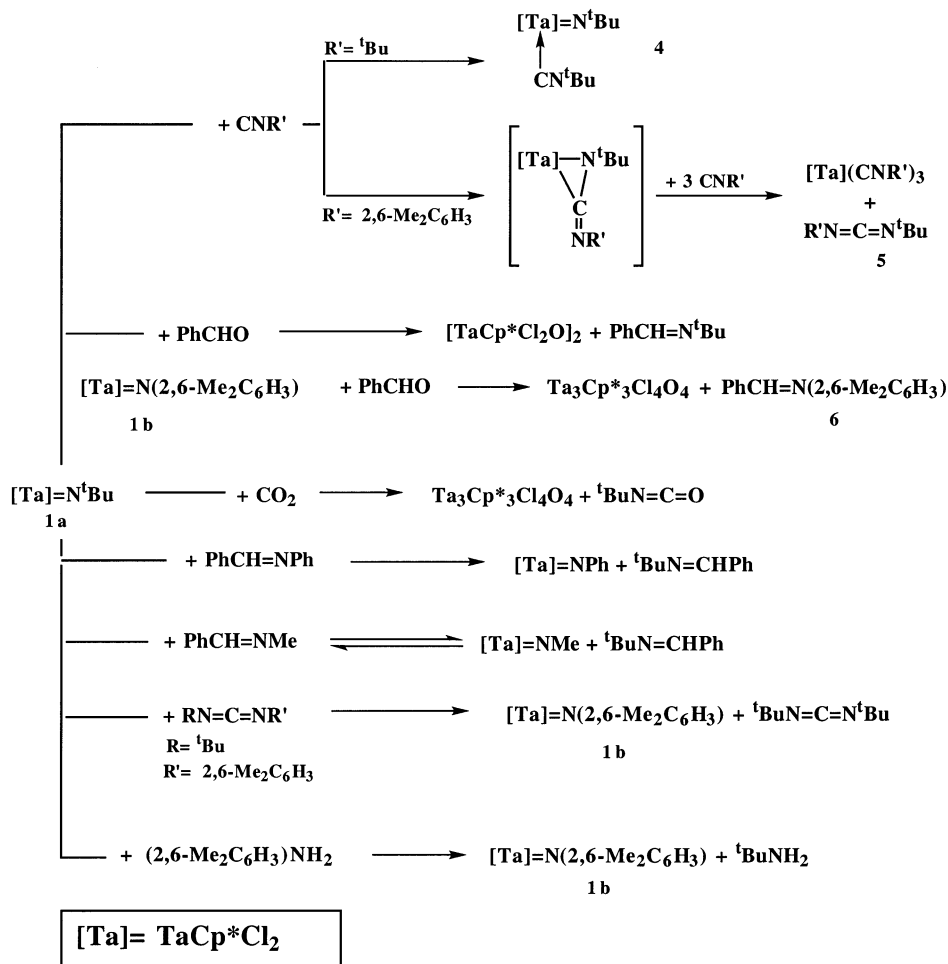
2.2. Reactions with isocyanides

The imido complex $[\text{TaCp}^*\text{Cl}_2(\text{N'Bu})]$ (**1a**) coordinated the isocyanide CN'Bu to give the 18-electron complex $[\text{TaCp}^*\text{Cl}_2(\text{N'Bu})(\text{CN'Bu})]$ (**4**) as a yellow solid, stable at room temperature under an inert atmosphere and also stable in solution. The formation of complex **4** and its structural behavior is analogous to that reported for related niobium and tantalum adducts [16]. The isocyanide ligand dissociated on heating a hexane solution of **4** to 140°C , leaving the starting compound **1a** and an unidentified residue.

However, a different rapid reaction took place when complex **1a** was treated with four equivalents of



Scheme 1.



Scheme 2.

CN(2,6-Me₂C₆H₃) to afford the tantalum(III) complex [TaCp*Cl₂{CN(2,6-Me₂C₆H₃)₃}] [17] with simultaneous elimination of the carbodiimide ^tBuN=C=N(2,6-Me₂-C₆H₃) (**5**) (see Scheme 2). This behavior reveals that the higher electrophilic character of the coordinated aryl isocyanide carbon atom favors nucleophilic attack on the *tert*-butyl imido nitrogen to give an intermediate η²-coordinated carbodiimide complex similar to those reported for related zirconium [5c] and iridium [5b] complexes, although its formation could not be detected in solution by ¹H-NMR spectroscopy. In the presence of three equivalents excess of the isocyanide, the diimide is reductively eliminated to give the final 18-electron tantalum(III) complex. The same reaction using one equivalent of the isocyanide in the presence of three equivalents of other ligands (THF, PMe₃) or using less than three equivalents of isocyanide gave mixtures containing varying amounts of the unreacted starting complex and final products. No reaction was observed when the starting complex **1a** was added to a solution containing the tantalum(III) complex. Carbodiimides have also been synthesized by coupling iso-

cyanates with elimination of CO₂, using phosphine oxides [18] and imido vanadium [10] or tungsten [6a] compounds as catalysts.

The aryl imido complex [TaCp*Cl₂{N(2,6-Me₂-C₆H₃)}] (**1b**), which has a much less nucleophilic imido nitrogen atom due to the aromatic aryl substituent, did not react with any of the isocyanide ligands, probably also due to the protecting bulkier aryl group which hinders an interaction with the vacant metal orbital [16c].

The chemical behavior of complexes **1a** and **1b** was also studied in reactions with CO and RCN (R = Me, Ph). No reaction was observed after heating benzene-*d*₆ solutions of both complexes in sealed tubes at 240°C for several hours, the unchanged starting reagents being recovered.

2.3. Reactions with benzaldehyde (PhCHO)

Both imido complexes **1a** and **1b** reacted with one equivalent of PhCHO to give the [2 + 2] cycloaddition [19] products, which could not be detected in solution

as they were rapidly transformed by elimination of imine PhCH=NR ($R = \text{'Bu}$ [20], 2,6- $\text{Me}_2\text{C}_6\text{H}_3$ (**6**)) and transfer of the oxo group to the metal (Scheme 2). The reaction of complex **1a** with the more nucleophilic *tert*-butyl imido ligand was complete after 4 h at room temperature eliminating PhCH=N'Bu and the resulting $[\text{TaCp}^*\text{Cl}_2(\text{O})]'$ fragment dimerized to give $[\text{TaCp}^*\text{Cl}_2(\text{O})]_2$ [21], whereas complex **1b** with a less nucleophilic aryl imido ligand reacts more slowly, the reaction being complete after 12 h at room temperature (or 1 h at 90°C). Under these conditions the resulting $[\text{TaCp}^*\text{Cl}_2(\text{O})]'$ fragment was hydrolytically transformed into the trimer $[(\text{TaCp}^*\text{Cl})_3(\mu^2\text{-Cl})(\mu^2\text{-O})_3(\mu^3\text{-O})]$ [21,22]. Both imines were recovered by chromatography and characterized by NMR spectroscopy.

2.4. Reaction with carbon dioxide (CO_2)

Reactions of C_6D_6 solutions of complexes **1a** and **1b** were studied in sealed NMR tubes filled with dry CO_2 and monitored by ^1H -NMR spectroscopy. Reaction of complex **1a** with the more electrophilic imido ligand started at 90°C and was complete after heating the tube to 140°C for 12 h to give a ^1H -NMR spectrum with signals due to the oxotantalum trimer [22] and the isocyanate 'BuN=C=O , formed by addition of CO_2 to the Ta–N bond [11b,23] (see Scheme 2). Formation of the intermediate O,O'-carbamate complex [23a] was not observed. The same reaction using the aryl imido complex **1b** was slower and not observed below 80°C, always giving a mixture of components which could not be determined by the ^1H -NMR spectra.

2.5. Reaction with *N*-benzylideneimines (PhCH=NR , $R = \text{Ph, Me}$)

The reaction of a C_6D_6 solution of complex **1a** with one equivalent of PhCH=NPh was monitored in a sealed NMR tube by ^1H -NMR spectroscopy (Scheme 2). No reaction was observed at room temperature, and there was a very slow reaction on heating to 165°C which was complete after 4 days. The resulting ^1H -NMR spectrum showed characteristic resonances due to the known [17] imido complex $[\text{TaCp}^*\text{Cl}_2(\text{NPh})]$ and the reported *N*-benzylidenetert-butylamine PhCH=N'Bu [20]. It follows that the reaction comprised exchange of a more-donating by a less-donating Ta=NR imido group through [2 + 2] cycloaddition of the starting imine, leading to the intermediate formation of a 2,4-diazametallacyclobutane [5d,e,6c,d], which could not be observed. When excess *N*-benzylideneaniline was used, the reaction was complete at 120 and 100°C when the molar ratios were 1/7 and 1/30, respectively.

The temperature and time required to complete the exchange reaction decreased (100°C, 48 h) when CDCl_3

was used as solvent. An equilibrium was observed when PhCH=NMe was used, leading after 3 days at 100°C in C_6D_6 to a mixture containing the starting materials, the amido complex $[\text{TaCp}^*\text{Cl}_2(\text{NMe})]$ [24] and the imine PhCH=N'Bu [20]. CDCl_3 is not recommended because overlapping resonances in the NMR spectra militate against adequate spectral analysis.

2.6. Reaction with carbodiimide

$[\text{N'Bu=C=N}(2,6\text{-Me}_2\text{C}_6\text{H}_3)]$

Complex **1a** reacted with one equivalent of (2,6- $\text{Me}_2\text{C}_6\text{H}_3$) N=C=N'Bu in a sealed NMR tube with exchange of the imido groups to give the imido complex **1b** and 'BuN=C=N'Bu after 12 h at 190°C. Formation of the intermediate tantalum derivative containing the triazamethylenemethane ligand [23a,25] formed by a [2 + 2] cycloaddition of the carbodiimide could not be observed as spontaneous metathesis gave the imido complex containing the less-basic imido group.

2.7. Reaction with amine RNH_2 ($R = 2,6\text{-Me}_2\text{C}_6\text{H}_3$)

Reaction of complex **1a** containing the more-basic N'Bu imido group with the less basic RNH_2 amine at 135°C for 8 days resulted in a similar exchange [26] with elimination of the more basic 'BuNH_2 amine to give complex $[\text{TaCp}^*\text{Cl}_2\{\text{N}(2,6\text{-Me}_2\text{C}_6\text{H}_3)\}]$ (**1b**), containing the less basic imido substituent (see Scheme 2).

2.8. C–H bond activation reactions

The formally 16-electron imido complexes **1a** and **1b** cannot activate C–H bonds. However, the methyl derivative $[\text{TaCp}^*\text{Me}(\text{N'Bu})(\text{NH'Bu})]$, obtained by reaction of the chloro methyl complex with LiNH'Bu [27], gave the aryl compound $[\text{TaCp}^*\text{Ph}(\text{N'Bu})(\text{NH'Bu})]$ (**7**), and a mixture of $[\text{TaCp}^*\text{R}(\text{N'Bu})(\text{NH'Bu})]$ ($R = m\text{-MeC}_6\text{H}_4$ (**8a**), $p\text{-MeC}_6\text{H}_4$ (**8b**)) when heated at 220°C in benzene and toluene, respectively, with evolution of methane (see Scheme 3). These products resulted from activation of one ring $\text{Csp}^2\text{-H}$ bond by the bis-imido derivative $[\text{TaCp}^*(\text{N'Bu})_2]'$, which could not be trapped by addition of bases such as THF, pyridine or Et_2O and whose formation could not be detected.

No C–H bond activation was observed when cyclohexane was used as solvent [28], although the bis-amido compound $[\text{TaCp}^*(\text{N'Bu})(\text{NH'Bu})_2]$ (**3**) was the major reaction product, probably resulting from intermolecular rearrangement and decomposition in a dimethyl complex $[\text{TaCp}^*\text{Me}_2(\text{N'Bu})]$ simultaneously formed.

The new *m*- and *p*-toluoyl complexes were obtained as an unresolvable mixture containing **8a/8b** in a molar ratio of ca. 1/4, deduced from the relative intensity of the methyl and ring proton signals observed in its

^1H -NMR spectrum in C_6D_6 . The presence of the corresponding *o*-toluoyl complex was not observed.

The ^1H -NMR spectrum of the aryl complex **7** shows the amido proton resonance at δ 5.71, whereas two resonances were observed at δ 5.59 and δ 5.60 for **8a** and **8b**, respectively, and a unique $\nu(\text{NH})$ IR absorption appeared at 3320 cm^{-1} . The ^{13}C -NMR spectra of the aryl complexes **7–8** show the expected resonances due to the quaternary ^tBu carbon of the amido and imido groups at ca. δ 55 and δ 65, respectively, and the signal due to the tantalum bound C_{ipso} between δ 181.3 and δ 185.9.

3. Conclusions

The imido tantalum complex $[\text{TaCp}^*\text{Cl}_2(\text{N}^t\text{Bu})]$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) coordinates CN^tBu to give the 18-electron adduct $[\text{TaCp}^*\text{Cl}_2(\text{N}^t\text{Bu})(\text{CN}^t\text{Bu})]$ but reacts with $\text{CN}(2,6\text{-Me}_2\text{C}_6\text{H}_3)$ with reductive transfer of the imido moiety to give the carbodiimide $^t\text{BuN}=\text{C}=\text{N}(2,6\text{-Me}_2\text{C}_6\text{H}_3)$ and the tantalum(III) derivative $[\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_2\{\text{CN}(2,6\text{-Me}_2\text{C}_6\text{H}_3)\}_3]$. Similar reactions did not take place with the related complex $[\text{TaCp}^*\text{Cl}_2\{\text{N}(2,6\text{-Me}_2\text{C}_6\text{H}_3)\}]$ containing a less nucleophilic imido ligand. The imido complexes also react with PhCHO , CO_2 and PhCHNR ($\text{R} = \text{Ph}$, Me) through a $[2+2]$ cycloaddition to give respectively the keteneimine and benzimine products resulting from exchange of the oxo by the imine group and the imine by a more electronegative imine substituent under appropriate conditions. The less-basic $\text{N}(2,6\text{-Me}_2\text{C}_6\text{H}_3)$ imido group is much less reactive.

The methyl complex $[\text{TaCp}^*\text{Me}(\text{N}^t\text{Bu})(\text{NH}^t\text{Bu})]$ activates benzene and toluene C–H bonds when heated at 220°C to give the aryl compounds $[\text{TaCp}^*\text{R}(\text{N}^t\text{Bu})(\text{NH}^t\text{Bu})]$ ($\text{R} = \text{Ph}$, *m*- MeC_6H_4 , *p*- MeC_6H_4). This reactivity is lower than that found for related more-electrophilic tantalum complexes.

4. Experimental

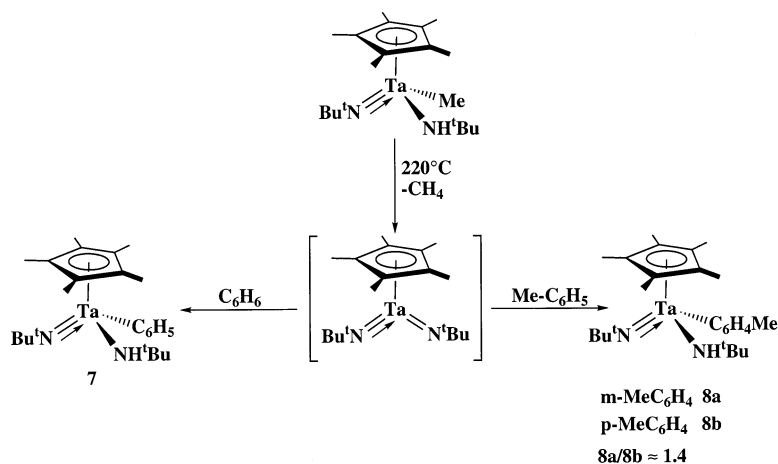
4.1. General methods

All manipulations were performed under inert atmosphere of argon using standard Schlenk techniques or a dry box. Solvents used were previously dried and freshly distilled under argon: tetrahydrofuran (THF) from sodium benzophenone ketyl; toluene from sodium; hexane and pentane from sodium–potassium alloy. Unless otherwise stated, reagents were obtained from commercial sources and used as received. Thermal reactions were carried out in a Roth autoclave with a regulated temperature between 20 and 300°C .

IR spectra were recorded in KBr pellets, over the range $4000\text{--}200\text{ cm}^{-1}$ on a Perkin–Elmer 583 spectrophotometer. ^1H - and ^{13}C -NMR spectra were recorded on a Varian Unity VXR-300. Chemical shifts, in ppm, are measured relative to residual ^1H and ^{13}C resonances of solvents: 7.15 (^1H , C_6D_6), 7.24 (^1H , CDCl_3), and 128.0 (^{13}C , C_6D_6) and 77.0 (^{13}C , CDCl_3), and coupling constants are in Hz. C, H and N analyses for all new compounds were carried out with a Perkin–Elmer 240 C microanalyzer.

4.2. Synthesis of $[\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_2(\text{N}^t\text{Bu})]$ (**1a**)

A solution of LiNH^tBu (1.19 g, 15.06 mmol) in Et_2O (40 ml) was added slowly at room temperature (r.t.) to a suspension of $[\text{TaCp}^*\text{Cl}_4]$ (3.00 g, 6.55 mmol) in Et_2O (30 ml) and the mixture was stirred for 12 h. SiClMe_3 (one equivalent) was then added and after 12 h of stirring the solvent was removed under vacuum and the residue was extracted into hexane ($2 \times 50\text{ ml}$). The solution was filtered and the volatiles were removed to yield **1a** as a yellow oil (2.16 g, 72%). ^1H -NMR (CDCl_3 , δ , ppm): 1.21 (s, 9H, N^tBu), 2.21 (s, 15H, C_5Me_5).



Scheme 3.

4.3. Synthesis of $[Ta(\eta^5-C_5Me_5)Cl_2\{N(2,6-Me_2C_6H_3)\}]$ (**1b**)

A solution of $LiNH(2,6-Me_2C_6H_3)$ (1.67 g, 13.10 mmol) in Et_2O (50 ml) was added slowly at r.t. to a suspension of $[TaCp^*Cl_4]$ (3.00 g, 6.55 mmol) in Et_2O (30 ml) and the mixture was stirred for 12 h. The solution was filtered and volatiles were removed to give **1b** as an orange solid, which was washed with hexane (30 ml) and dried under vacuum (2.68 g, 81%). 1H -NMR ($CDCl_3$, δ , ppm): 2.17 (s, 15H, C_5Me_5), 2.35 (s, 6H, $Me_2C_6H_3$), 6.62 (t, $J = 7.65$ Hz, $1H_{para}$, $Me_2C_6H_3$), 6.96 (d, $J = 7.65$ Hz, $2H_{meta}$, $Me_2C_6H_3$).

4.4. Synthesis of $[Ta(\eta^5-C_5Me_5)Cl(N^iBu)(NH^iBu)]$ (**2**)

A solution of $LiNH^iBu$ (0.51 g, 6.55 mmol) in Et_2O (25 ml) was added slowly at r.t. to a suspension of $[TaCp^*Cl_4]$ (1.00 g, 2.18 mmol) in Et_2O (15 ml) and the mixture was stirred overnight. The solvent was removed under vacuum and the residue was extracted into hexane (40 ml) to give a solution which was then filtered. Complex **2** was isolated as a yellow oil after removing the volatiles under vacuum. IR (KBr, ν , cm^{-1}): 3330 (w, N–H), 1269 (s, Ta=N). 1H -NMR ($CDCl_3$, δ , ppm): 1.22 (s, 18 H, Ta=NⁱBu and NHⁱBu), 2.07 (s, 15 H, C_5Me_5), 5.64 (s, 1 H, NH). ^{13}C -NMR ($CDCl_3$, δ , ppm): 11.6 (C_5Me_5), 33.3 (CMe_3), 34.3 (CMe_3), 55.7 (NHCMe₃), 65.0 (Ta=NCMe₃), 116.8 (C_5Me_5). Anal. Calc. for $C_{18}H_{34}ClN_2Ta$: C, 43.68; H, 6.94; N, 5.66%. Found: C, 42.98; H, 6.51; N, 5.33%.

4.5. Synthesis of $[Ta(\eta^5-C_5Me_5)(N^iBu)(NH^iBu)_2]$ (**3**)

A solution of $LiNH^iBu$ (1.42 g, 18.00 mmol) in Et_2O (50 ml) was added slowly at r.t. to a suspension of $[TaCp^*Cl_4]$ (2.00 g, 4.37 mmol) in Et_2O (20 ml) and the mixture was stirred overnight. The solvent was removed under vacuum and the residue was extracted into hexane (50 ml). After filtration the volatiles were removed to yield **3** as a white solid (1.97 g, 85%). IR (KBr, ν , cm^{-1}): 3326 (w, N–H), 1264 (s, Ta=N). 1H -NMR ($CDCl_3$, δ , ppm): 1.20 (s, 18H, NHⁱBu), 1.27 (s, 9H, Ta=NⁱBu), 1.99 (s, 15H, C_5Me_5), 3.01 (s, 2H, NH). ^{13}C -NMR ($CDCl_3$, δ , ppm): 11.6 (C_5Me_5), 33.9 (Ta=NCMe₃), 35.1 (NHCMe₃), 53.7 (NHCMe₃), 64.4 (Ta=NCMe₃), 114.3 (C_5Me_5). Anal. Calc. for $C_{22}H_{44}N_3Ta$: C, 49.70; H, 8.36; N, 7.91%. Found: C, 49.72; H, 8.11; N, 7.56%.

4.6. Synthesis of $[Ta(\eta^5-C_5Me_5)Cl_2(N^iBu)(CN^iBu)]$ (**4**)

Isocyanide ⁱBuNC (0.65 mmol) was added to a solution of $[TaCp^*Cl_2(N^iBu)]$ (**1a**) (0.25 g, 0.53 mmol) in hexane (10 ml) at r.t. The solution quickly became cloudy and after 2 h stirring was stopped and the

solvent was filtered off to give **4** as a yellow solid, which was washed with pentane and dried under vacuum (0.24 g, 84%). IR (KBr, ν , cm^{-1}): 2200 (s, CN), 1350 (m, TaN). 1H -NMR ($CDCl_3$, δ , ppm): 1.18 (s, 9H, ⁱBu), 1.55 (s, 9H, CNⁱBu), 2.14 (s, 15H, C_5Me_5). ^{13}C -NMR ($CDCl_3$, δ , ppm): 12.15 (C_5Me_5), 29.82 (CMe_3), 32.16 (CMe_3), 57.67 (CMe_3), 67.46 (CMe_3), 119.10 (C_5Me_5), 151.15 (ⁱBuNC). Anal. Calc. for $C_{19}H_{33}Cl_2N_2Ta$: C, 42.15; H, 6.16; N, 5.18. Found: C, 42.20; H, 6.14; N, 5.09%.

4.7. Reaction of $[TaCp^*Cl_2(N^iBu)]$ with $CN(2,6-Me_2C_6H_3)$. Synthesis of $[TaCp^*Cl_2\{CN(2,6-Me_2C_6H_3)\}_3]$ and ⁱBuN=C=N(2,6-Me₂C₆H₃) (**5**)

Isocyanide $CN(2,6-Me_2C_6H_3)$ (1.20 g, 9.15 mmol) was added to a solution of $[TaCp^*Cl_2(N^iBu)]$ (**1a**) (1.00 g, 2.18 mmol) in hexane (25 ml) and the mixture was stirred for 1 h at r.t. The color changed from yellow to dark red leaving a red solid, which was separated by filtration and washed with hexane (2 × 20 ml) to be characterized as the reported tantalum(III) complex (1.53 g, 90%). 1H -NMR (C_6D_6 , δ , ppm): 2.14 (s, 15H, C_5Me_5), 2.51 (s, 6H, 2,6-Me₂C₆H₃), 2.53 (s, 12H, 2,6-Me₂C₆H₃), 6.60–6.90 (m, 9H, 2,6-Me₂C₆H₃). The solution was passed through a column of silica gel and then eluted with THF to give a solution, which after removal of the solvent under reduced pressure rendered a colorless solid identified as ⁱBuN=C=N(2,6-Me₂C₆H₃) (**5**) (0.35 g, 79%). 1H -NMR ($CDCl_3$, δ , ppm): 1.36 (s, 9H, CMe_3), 2.34 (s, 6H, 2,6-Me₂C₆H₃), 6.70–6.80 (m, 3H, 2,6-Me₂C₆H₃). ^{13}C -NMR ($CDCl_3$, δ , ppm): 19.03 (2,6-Me₂C₆H₃), 31.33 (CMe_3), 45.06 (CMe_3), 123.96, 128.04, 132.31, 137.01 (2,6-Me₂C₆H₃), 296.85 (NCN).

4.8. Reaction of $[TaCp^*Cl_2(N^iBu)]$ with $PhCHO$

A solution of $[TaCp^*Cl_2(N^iBu)]$ (**1a**) (0.50 g, 1.09 mmol) and $PhCHO$ (1.30 mmol) in hexane (15 ml) was stirred for 4 h at r.t. The suspension was allowed to settle and filtered, leaving a yellow solid that was identified as $[TaCp^*Cl_2(O)]_2$ (0.40 g, 90%). 1H -NMR (C_6D_6 , δ , ppm): 2.22 (C_5Me_5).

The resulting solution was passed through a silica gel column and eluted with THF. The volatile components were removed under vacuum and $PhCH=N^iBu$ was obtained as a white oil (0.15 g, 78%). 1H -NMR ($CDCl_3$, δ , ppm): 1.36 (s, 9H, CMe_3), 7.40–7.45 (m, 3H, C_6H_5), 7.78–7.84 (m, 2H, C_6H_5), 8.32 (s, 1H, N=CH).

4.9. Reaction of $[TaCp^*Cl_2\{N(2,6-Me_2C_6H_3)\}]$ with $PhCHO$

A mixture of $[TaCp^*Cl_2\{N(2,6-Me_2C_6H_3)\}]$ (**1b**) (0.50 g, 0.99 mmol) and $PhCHO$ (1.15 mmol) in toluene

(15 ml) was stirred for 12 h at r.t. (or for 6 h at 90°C), the color changed from orange to yellow. The solvent was then removed under vacuum and *n*-hexane (15 ml) was added. The suspension was allowed to settle and filtered leaving a yellow solid, which was identified as $[\text{Ta}_3\text{Cp}_3^*\text{Cl}_4\text{O}_4]$ (0.30 g, 81%). $^1\text{H-NMR}$ (CDCl_3 , δ , ppm): 2.23 (s, 15 H, C_5Me_5), 2.21 (s, 30 H, C_5Me_5).

The resulting solution was passed through a silica gel column and eluted with THF. After removing the volatile components $\text{PhCH}=\text{N}(2,6\text{-Me}_2\text{C}_6\text{H}_3)$ (**6**) was obtained as a white oil (0.17 g, 85%). $^1\text{H-NMR}$ (CDCl_3 , δ , ppm): 2.13 (s, 6H, $2,6\text{-Me}_2\text{C}_6\text{H}_3$), 6.91–7.05 (m, 3H, $2,6\text{-Me}_2\text{C}_6\text{H}_3$), 7.45 (m, 3H, C_6H_5), 7.88 (m, 2H, C_6H_5), 8.21 (s, 1H, $\text{N}=\text{CH}$). $^{13}\text{C-NMR}$ (CDCl_3 , δ , ppm): 18.2 ($2,6\text{-Me}_2\text{C}_6\text{H}_3$), 127.2, 128.0, 128.6, 128.9, 129.70, 131.6, 134.4, 135.8 ($2,6\text{-Me}_2\text{C}_6\text{H}_3$ and C_6H_5), 162.8 ($\text{C}=\text{N}$).

4.10. Reaction of $[\text{TaCp}^*\text{Cl}_2(\text{N}^i\text{Bu})]$ with CO_2

An NMR tube was charged with a solution of $[\text{TaCp}^*\text{Cl}_2(\text{N}^i\text{Bu})]$ (**1a**) in C_6D_6 and sealed under CO_2 . The $^1\text{H-NMR}$ showed no change until the tube was heated at 100°C. The reaction was complete after 12 h at 140°C giving $[\text{Ta}_3\text{Cp}_3^*\text{Cl}_4\text{O}_4]$ (78% by NMR) and $^i\text{BuNCO}$ (92% by NMR). $^1\text{H-NMR}$ (C_6D_6 , δ , ppm): 0.90 (CMe_3).

4.11. Reaction of $[\text{TaCp}^*\text{Cl}_2(\text{N}^i\text{Bu})]$ with $\text{PhCH}=\text{NPh}$

An NMR tube was charged with a solution of $[\text{TaCp}^*\text{Cl}_2(\text{N}^i\text{Bu})]$ (**1a**) (0.010 g, 2.18×10^{-5} mol) and $\text{PhCH}=\text{NPh}$ (2.20×10^{-5} mol) in C_6D_6 . The $^1\text{H-NMR}$ spectrum did not show a change until the tube was heated at 165°C in an autoclave; the reaction was complete after 5 days to give $\text{PhCH}=\text{N}^i\text{Bu}$ and $[\text{TaCp}^*\text{Cl}_2(\text{NPh})]$ (93% by NMR). $^1\text{H-NMR}$ (C_6D_6 , δ , ppm): 1.85 (s, 15H, C_5Me_5), 6.77 (t, 1H, C_6H_5), 6.96 (d, 2H, C_6H_5), 7.23 (t, 2H, C_6H_5).

4.12. Reaction of $[\text{TaCp}^*\text{Cl}_2(\text{N}^i\text{Bu})]$ with $\text{PhCH}=\text{NMe}$

An NMR tube was charged with a solution of $[\text{TaCp}^*\text{Cl}_2(\text{N}^i\text{Bu})]$ (**1a**) (0.010 g, 2.18×10^{-5} mol) and $\text{PhCH}=\text{NMe}$ (2.20×10^{-5} mol) in C_6D_6 . The $^1\text{H-NMR}$ spectrum did not show a change until the tube was heated at 80°C, reaching an equilibrium mixture of **1a**, imine $\text{PhCH}=\text{NMe}$, $[\text{TaCp}^*\text{Cl}_2(\text{NMe})]$ and $\text{PhCH}=\text{N}^i\text{Bu}$.

4.13. Reaction of $[\text{TaCp}^*\text{Cl}_2(\text{N}^i\text{Bu})]$ with $\text{NH}_2(2,6\text{-Me}_2\text{C}_6\text{H}_3)$

An NMR tube was charged with a solution of $[\text{TaCp}^*\text{Cl}_2(\text{N}^i\text{Bu})]$ (**1a**) (0.010 g, 2.18×10^{-5} mol) and $\text{NH}_2(2,6\text{-Me}_2\text{C}_6\text{H}_3)$ (2.18×10^{-5} mol) in C_6D_6 . The

$^1\text{H-NMR}$ did not show a change until the tube was heated at 135°C; the reaction was complete after 8 days with the formation of $^i\text{BuNH}_2$ and $[\text{TaCp}^*\text{Cl}_2\{\text{N}(2,6\text{-Me}_2\text{C}_6\text{H}_3)\}]$ (**1b**) (>95% by NMR). $^1\text{H-NMR}$ (C_6D_6 , δ , ppm): 1.83 (s, 15H, C_5Me_5), 2.45 (s, 6H, $2,6\text{-Me}_2\text{C}_6\text{H}_3$), 6.66 (t, 1H, C_6H_5), 6.96 (d, 2H, C_6H_5).

4.14. Reaction of $[\text{TaCp}^*\text{Cl}_2(\text{N}^i\text{Bu})]$ with $^i\text{BuN}=\text{C}=\text{N}(2,6\text{-Me}_2\text{C}_6\text{H}_3)$

An NMR tube was charged with a solution of $[\text{TaCp}^*\text{Cl}_2(\text{N}^i\text{Bu})]$ (**1a**) (0.010 g, 2.18×10^{-5} mol) and $^i\text{BuN}=\text{C}=\text{N}(2,6\text{-Me}_2\text{C}_6\text{H}_3)$ (2.20×10^{-5} mol) in C_6D_6 . The $^1\text{H-NMR}$ did not show a change until the tube was heated at 180°C in an autoclave; the reaction was complete after 10 h at 190°C with the formation of $[\text{TaCp}^*\text{Cl}_2\{\text{N}(2,6\text{-Me}_2\text{C}_6\text{H}_3)\}]$ (**1b**) and $^i\text{BuN}=\text{C}=\text{N}^i\text{Bu}$ (80% by NMR). $^1\text{H-NMR}$ (C_6D_6 , δ , ppm): 1.16 (s, 18H, ^iBu).

4.15. Synthesis of $[\text{TaCp}^*\text{Ph}(\text{N}^i\text{Bu})(\text{NH}^i\text{Bu})]$ (**7**)

A solution of $[\text{TaCp}^*\text{Me}(\text{N}^i\text{Bu})(\text{NH}^i\text{Bu})]$ (2.0 g, 4.22 mmol) in C_6H_6 (15 ml) was heated in an autoclave for 3 days at 220°C. The volatiles were then removed under vacuum, hexane (2×30 ml) was added and the solution was filtered. Removal of solvents to 5 ml and cooling at -20°C yielded **7** as a white solid (1.72 g, 76%). IR (KBr, ν , cm^{-1}): 3318 (w, N–H), 1268 (s, Ta=N). $^1\text{H-NMR}$ (CDCl_3 , δ , ppm): 1.24 (s, 18H, CMe_3), 1.93 (s, 15H, C_5Me_5), 5.71 (s, 1H, NH), 6.99 (t, $J = 6.9$ Hz, 1H_{para} , C_6H_5), 7.10 (m, 2H_{meta} , C_6H_5), 7.41 (d, $J = 6.6$ Hz, 2H_{ortho} , C_6H_5). $^{13}\text{C-NMR}$ (CDCl_3 , δ , ppm): 11.5 (C_5Me_5), 33.6 (CMe_3), 34.6 (CMe_3), 55.6 (NHCMe_3), 64.8 (Ta=NCMe₃), 115.3 (C_5Me_5), 124.4, 126.5, 141.4, 185.9 (C_6H_5). Anal. Calc. for $\text{C}_{24}\text{H}_{39}\text{N}_2\text{Ta}$: C, 53.73; H, 7.33; N, 5.22. Found: C, 53.79; H, 7.16; N, 5.15%.

4.16. Synthesis of $[\text{TaCp}^*\text{R}(\text{N}^i\text{Bu})(\text{NH}^i\text{Bu})]$ ($\text{R} = m\text{-MeC}_6\text{H}_4$ (**8a**), $p\text{-MeC}_6\text{H}_4$ (**8b**))

A solution of $[\text{TaCp}^*\text{Me}(\text{N}^i\text{Bu})(\text{NH}^i\text{Bu})]$ (2.0 g, 4.22 mmol) in toluene (15 ml) was treated by the procedure described in Section 4.15 to yield a white solid, which was identified as a mixture of **8a** and **8b** (total yield 1.81 g, 78%). IR (KBr, ν , cm^{-1}): 3320 (w, N–H), 1272 (s, Ta=N). $^1\text{H-NMR}$ (CDCl_3 , δ , ppm): 1.24 (s, 36H, CMe_3), 1.92 (s, 30H, C_5Me_5), 2.24 (s, 6H, MeC_6H_4), 5.59 (s, 1H, NH), 5.60 (s, 1H, NH), 6.80 (**8a**, d, $J = 7.3$ Hz, 1H_{para} , MeC_6H_4), 7.00 (**8a**, m, 1H_{meta} , MeC_6H_4), 7.19 (**8a**, d, $J = 7.3$ Hz, 1H_{ortho} , MeC_6H_4), 7.25 (**8a**, s, 1H_{ortho} , MeC_6H_4), 6.92 (**8b**, d, $J = 7.5$ Hz, 2H_{meta} , MeC_6H_4), 7.29 (**8b**, d, $J = 7.5$ Hz, 2H_{ortho} , MeC_6H_4). $^{13}\text{C-NMR}$ (CDCl_3 , δ , ppm): 11.5 (C_5Me_5), 21.4 (MeC_6H_4), 21.8 (MeC_6H_4), 33.6 (CMe_3), 34.6 (CMe_3), 55.6 (NHCMe_3), 64.8 (Ta=NCMe₃), 115.3 (C_5Me_5),

125.3, 126.2, 127.5, 133.7, 135.2, 138.3, 141.3, 142.2, 181.3, 185.8 (MeC₆H₄). Anal. Calc. for C₂₄H₃₉N₂Ta: C, 54.54; H, 7.51; N, 5.09. Found: C, 54.80; H, 7.48; N, 5.00%.

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References

- [1] (a) W.A. Nugent, J.M. Mayer, *Metal Ligand Multiple Bonds*, Wiley Interscience, New York, 1988. (b) D.E. Wigley, *Prog. Inorg. Chem.* 42 (1994) 239.
- [2] K.I. Ivin, *Olefin Metathesis*, Academic Press, London, 1983.
- [3] R.R. Schrock, in: D.J. Brunelle (Ed.), *Ring Opening Polymerization*, C. Hanser Verlag, Munich, 1993.
- [4] (a) D.A. Evans, M.M. Faul, M.T.B. Blodeau, *J. Org. Chem.* 56 (1991) 6744. (b) Y.-W. Ge, P.R. Sharp, *Inorg. Chem.* 31 (1992) 379. (c) P.L. Mcgrane, T.J. Livinghouse, *Org. Chem.* 57 (1992) 1323. (d) P.L. Mcgrane, M. Jensen, T.J. Livinghouse, *Am. Chem. Soc.* 114 (1992) 5459.
- [5] (a) P.J. Walsh, F.J. Hollander, R.G. Bergman, *J. Am. Chem. Soc.* 110 (1988) 8729. (b) D.S. Glueck, F.J. Hollander, R.G. Bergman, *J. Am. Chem. Soc.* 111 (1989) 2719. (c) P.J. Walsh, F.J. Hollander, R.G. Bergman, *Organometallics* 12 (1993) 3705. (d) K.E. Meyer, P.J. Walsh, R.G. Bergman, *J. Am. Chem. Soc.* 116 (1994) 2669. (e) K.E. Meyer, P.J. Walsh, R.G. Bergman, *J. Am. Chem. Soc.* 117 (1995) 974. (f) S.Y. Lee, R.G. Bergman, *J. Am. Chem. Soc.* 118 (1996) 6396.
- [6] (a) I. Meisel, G. Hertel, K. Weiss, *J. Mol. Catal.* 36 (1986) 159. (b) M.L.H. Green, G. Hogarth, P.C. Konidaris, P. Mountford, *J. Organomet. Chem.* 394 (1990) C9. (c) G.K. Cantrell, T.Y. Meyer, *Chem. Commun. (Cambridge)* (1997) 1551. (d) G.K. Cantrell, T.Y. Meyer, *Organometallics* 16 (1997) 5382.
- [7] (a) C.C. Cummings, C.P. Schaller, G.D. van Duyne, P.T. Wolczanski, E.A.-W. Chan, R. Hoffmann, *J. Am. Chem. Soc.* 113 (1991) 2985. (b) J.L. Bennett, P.T. Wolczanski, *J. Am. Chem. Soc.* 116 (1994) 2179.
- [8] (a) A.M. Baranger, P.J. Walsh, R.G. Bergman, *J. Am. Chem. Soc.* 115 (1993) 2753. (b) C.C. Cummings, S.M. Baxter, P.T.J. Wolczanski, *Am. Chem. Soc.* 110 (1988) 8731. (c) C.P. Schaller, J.R. Bonnano, P.T.J. Wolczanski, *Am. Chem. Soc.* 116 (1994) 4133. (d) C.P. Schaller, C.C. Cummins, P.T.J. Wolczanski, *Am. Chem. Soc.* 118 (1996) 591.
- [9] (a) J. de With, A.D. Horton, *Angew. Chem. Int. Ed. Engl.* 32 (1993) 103. (b) J. de With, A.D. Horton, A.G. Orpen, *Organometallics* 12 (1993) 1493.
- [10] (a) K.R. Birdwhistell, T. Boucher, M. Enslinger, S. Harris, M. Johnson, S. Toporek, *Organometallics* 12 (1993) 1023. (b) K.R. Birdwhistell, J. Lanza, J.J. Pasos, *Organomet. Chem.* 584 (1999) 200.
- [11] (a) C.P. Schaller, P.T. Wolczanski, *Inorg. Chem.* 32 (1993) 131. (b) R.E. Blake, D.M. Antonelli, L.M. Henling, W.P. Schaefer, K.I. Hardcastle, J.E. Bercaw, *Organometallics* 17 (1998) 718.
- [12] (a) M.V. Galakhov, M. Gómez, G. Jiménez, P. Royo, M.A. Pellinghelli, A. Tiripicchio, *Organometallics* 14 (1995) 1901. (b) M. Gómez, P. Royo, *Bull. Pol. Acad. Sci. Chem.* 42 (1995) 422. (c) M.V. Galakhov, M. Gómez, G. Jiménez, P. Royo, *Organometallics* 14 (1995) 2843. (d) M. Gómez, P. Gómez-Sal, G. Jiménez, A. Martín, P. Royo, Sánchez-Nieves, *Organometallics* 15 (1996) 3579.
- [13] S. Schmidt, J. Sundermeyer, *J. Organomet. Chem.* 472 (1994) 127.
- [14] (a) D.J. Arney, M.A. Bruck, S.R. Huber, D.E. Wigley, *Inorg. Chem.* 31 (1992) 3749. (b) W. Herrmann, W. Baratta, E. Herdtweck, *Angew. Chem. Int. Ed. Engl.* 35 (1996) 1951.
- [15] (a) J.M. Mayer, C.J. Curtis, J.E.J. Bercaw, *Am. Chem. Soc.* 105 (1983) 2651. (b) Y.-W. Chao, P.A. Wexler, D.E. Wigley, *Inorg. Chem.* 20 (1990) 4592.
- [16] (a) M.I. Alcalde, J. de la Mata, M. Gómez, P. Royo, F.J. Sánchez, *Organomet. Chem.* 492 (1995) 151. (b) M.I. Alcalde, J. de la Mata, M. Gómez, P. Royo, M.A. Pellinghelli, A. Tiripicchio, *Organometallics* 13 (1994) 465. (c) D.N. Williams, J.P. Mitchell, A.D. Poole, U. Siemeling, W. Clegg, D.C.R. Hockless, P.A. O'Neil, V.C. Gibson, *J. Chem. Soc. Dalton Trans.* (1992) 739. (d) D.N. Williams, A.D. Poole, U. Siemeling, W. Clegg, D.C.R. Hockless, V.C. Gibson, *J. Organomet. Chem.* 462 (1993) C12.
- [17] M. Gómez, P. Gómez-Sal, M.P. Nicolás, P. Royo, *J. Organomet. Chem.* 491 (1995) 121.
- [18] (a) J.J. Monagle, T.W. Campbell, F.F. McShane, *J. Am. Chem. Soc.* 84 (1962) 4288. (b) T.W. Campbell, J.J. Monagle, V.S. Fold, *J. Am. Chem. Soc.* 84 (1962) 3673. (c) A. William, I.T. Ibrahim, *Chem. Rev.* 81 (1981) 589.
- [19] M. Jolly, J.P. Mitchell, V.C. Gibson, *J. Chem. Soc. Dalton Trans.* (1992) 1329.
- [20] T. Saka, T. Kadama, T. Fujimoto, K. Chita, I.J. Yamamoto, *Org. Chem.* 59 (1994) 7144.
- [21] V.C. Gibson, T.P. Kee, *J. Chem. Soc. Chem. Commun.* (1989) 656.
- [22] P.J. Jerkanoff, C.M. de Bellefon, G.L. Geoffroy, A.L. Rheingold, S.J. Geib, *Organometallics* 6 (1987) 1362.
- [23] (a) A.J. Blake, M.S. McInnes, P. Mountford, G.Z. Nikonov, D. Swallow, D.J. Watkin, *J. Chem. Soc. Dalton Trans.* (1999) 379 and references therein. (b) L. Kloppenburg, J.L. Petersen, *Organometallics* 15 (1996) 7.
- [24] M. Jolly, J.P. Mitchell, V.C. Gibson, *J. Chem. Soc. Dalton Trans.* (1992) 1331.
- [25] M.B. Dinger, W. Henderson, *Chem. Commun. (Cambridge)* (1996) 211.
- [26] (a) R.I. Michelman, R.G. Bergman, R.A. Andersen, *Organometallics* 12 (1993) 2741. (b) D.S. Glueck, S. Wu, F.J. Hollander, R.G. Bergman, *J. Am. Chem. Soc.* 113 (1991) 2041. (c) M.C.W. Chan, J.M. Cole, V.C. Gibson, J.A.K. Howard, *Chem. Commun. (Cambridge)* (1997) 2345.
- [27] P. Royo, J. Sánchez-Nieves, M.A. Pellinghelli, A. Tiripicchio, unpublished results.
- [28] B.R. Cook, T.J. Reinart, K.S. Suslick, *J. Am. Chem. Soc.* 108 (1986) 7281.